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TECHNICAL NOTE

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ELECTRON AND LIGHT MICROSCOPY TECHNIQUES SUITABLE
FOR STUDYING FATIGUE DAMAGE IN A
CRYSTALLIZED GLASS CERAMIC

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SUMMARY

The crystals of Pyroceram are randomly oriented and highly reflective so that standard microscopy techniques are not satisfactory for studying this material. Standard replicating procedures proved difficult to use. New microscopy techniques and procedures have therefore been developed. A method for locating, orienting, and identifying specific areas to be viewed with an electron microscope is described. This method does not require any special equipment.

Plastic replicas were found to be unsatisfactory because of their tendency to adhere to Pyroceram. This caused them to tear when released or resulted in artifacts. Preshadowed silicon monoxide replicas were satisfactory but required a releasing agent. A method of depositing the releasing agent is described.

To polish specimens without evidence of fire-polishing, it was found necessary to use a vibratory polishing technique. Chrome oxide was used as the abrasive and either water or kerosene as the lubricant. Vibratory polishing is extremely slow, but surfaces so polished show no evidence of fire polishing, even when examined by electron microscopy. The most satisfactory etching process used for Pyroceram 9608 consisted of a primary etch of 5 milliliters of hydrochloric acid (concentrated), 5 milliliters of hydrogen fluoride (45 percent), and 45 milliliters of water, and a secondary etch with methyl alcohol replacing the water. Best results were obtained with total etching times from 25 to 30 seconds.

Staining of the Pyroceram surface with a Sanford's marker was found to be an expedient way to reduce the glare of reflected light.

INTRODUCTION

As temperatures in bearings for application in aircraft, missiles, and space vehicles increase and approach 1000° F or greater, metal alloy bearings, for various reasons, become unsuitable. To meet the increasing need for bearing applications at temperatures above the maximum temperature at which alloy steels are useful, ceramics and cermets are being considered. Among these is a crystallized glass ceramic known commercially as Pyroceram 9608.

Pyroceram 9608 is essentially a glass base substance to which a nucleating agent has been added. The result is a crystalline phase in an amorphous matrix, the crystals being randomly oriented (refs. 1 and 2).

Research on rolling-contact fatigue at the Lewis Research Center (refs. 3 and 4) indicates that the fatigue characteristics of Pyroceram 9608 are similar to those of steels in that they both fail by spalling and these spalls are limited in area and depth of penetration. It would be most desirable to understand the exact mechanism by which cracks initiate and propagate in a bearing to form a spall or failure. In the case of steel ball specimens in rolling-contact fatigue, it is difficult to make studies of initial or incipient cracks by optical or electron microscopy techniques because failure propagation is rather rapid, and the material exhibits a wide range of failure times or scatter, making it difficult if not impossible to determine when incipient cracks form. Pyroceram ball specimens, however, exhibit relatively small differences in life from specimen to specimen. The rate of progression from the first incipient crack to a spall in this material is relatively slow as compared with steels. Also, incipient cracks (and thus initial spalling) occur at various locations in the running track of a specimen at approximately the same time. Therefore, the occurrence of incipient cracks and the extent of their propagation can be predicted and easily located in and around the running track of the specimen. Because of the preceding, Pyroceram is an ideal material to study fatigue from both an optical and electron microscope standpoint.

Preliminary work conducted by the Lewis Research Center indicated that the fine crystals in the Pyroceram reflected light in such a random way that neither petrographic techniques, transmitted light, reflected dark-ground illumination, nor reflected phase contrast can be employed to study this material. Standard polishing techniques, because of the high pressure and resulting friction, produce fire-polishing of the specimen surface. The result is surface flow of the material which tends to obliterate the structure for examination (refs. 5 to 8).

Attempts to study this material by the use of standard replicating procedures (ref. 9) proved difficult. Plastic replicas stick so tenaciously to the surface that they have a tendency to become overly distorted or torn when removed. Carbon and silicon monoxide replicas can

be removed from the surface by etching through them; but in such a case there is damage to the surface of the specimen. Then too, when it is desired to study particular fatigue cracks or areas, locating these areas under the electron microscope with standard techniques becomes a matter of chance and nearly impossible to achieve.

The object of this investigation is to present and describe polishing, etching, replication, and area-locating techniques that may be successfully used to study Pyroceram by optical and electron microscopy. Area-locating techniques would not only permit locating very minute cracks, defects, and microconstituents in Pyroceram, but also in other types of materials.

Pyroceram ball specimens, each with a running track that had been stressed in a rolling-contact fatigue apparatus, were selected for study. These specimens were examined after some degree of spalling had occurred. Polishing, etching, and replicating techniques were first developed to reveal the true microstructure of Pyroceram. Subsequently, the bulk of the efforts involved the development of methods for locating minute areas or defects.

MATERIAL, PROCEDURE, AND APPARATUS

Test Specimen Materials and Manufacture

Pyroceram is essentially a glass to which a nucleating agent, usually titanium dioxide, has been added. After casting and annealing, it closely resembles glass in all respects. Two heat-treating processes are required to change this glassy phase into Pyroceram. The first process is called nucleation; the second crystallization. These two heat-treating processes change the size and distribution of the Pyroceram crystals just as heat-treating processes may change the crystalline structure in metals. However, the formation of the crystals does not consume all the material of the batch (or melt). The result is a crystalline phase in an amorphous matrix, the crystals being randomly oriented (refs. 1 and 2).

Before heat treating, Pyroceram 9608 was cast into raw spherical blanks approximately 3/4 inch in diameter. After heat treating, the raw blanks were ground to finished 1/2-inch-diameter balls.

Mounting and Orienting Specimens for Metallographic Study

The specimens used were Pyroceram 9608 1/2-inch balls, each of which had a running track that had been exposed to repeated stresses in rolling contact. The material to be studied lay under the track that could be

outlined with a dye. Each specimen was mounted in Lucite so that the track orientation could be seen.

There were two specimen orientations adopted. In the first, the specimen was positioned in the mount so that a radial line extending from the center of the ball to a fully developed spall or fatigue failure in the ball running track was perpendicular to the polishing surface (fig. 1(a)). The other specimen orientation is shown in figure 1(b). Here the plane of the running track is parallel to the polishing surface. The advantage of orienting the ball specimen as in figure 1(a) would be to study the fatigue cracks emanating from the spalled or failed area, propagating parallel and below the running track. If the specimen is oriented as in figure 1(b), the incipient cracks are seen in longitudinal section and can be readily located without any spalling on the surface of the specimen.

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Apparatus

The NASA five-ball fatigue tester was used to stress these specimens in rolling contact. A description of this apparatus can be found in references 3 and 4. This type of fatigue tester produces the spalls and incipient cracks in the track of a ball being studied. The incipient cracks are of major concern in this study.

Standard light and electron microscopy equipment was used in all techniques and processes developed. These include a metallographic microscope fitted with a square mechanical stage and a transmission (light) microscope fitted with a circular stage and having phase contrast lenses.

RESULTS AND DISCUSSION

Specimen Polishing Techniques Developed

In polishing ceramics or glass by conventional methods, the heat developed by the friction between the abrasive and the sample has been shown to be sufficient to raise the temperature of a specific point of the sample to or above the melting point of the material (refs. 5 to 8). Such polishing is merely fire-polishing on a submicro scale. To eliminate this effect, the Pyrocera specimens were polished on a vibratory polisher that was set to give a maximum amplitude of approximately 0.06 inch. If a large volume of material had to be removed to reach an area to be studied, a rough polish was first used. The abrasive employed for this rough polish was synthetic sapphire, and the lubricant was either kerosene or water. When the area was reached, a final polish was used consisting of chromium oxide as the abrasive. Kerosene or water was again the lubricant. Where a small volume of material had to be

removed, only the final polish was used. Although slow, this process had not shown any fire-polishing effects even when the samples were examined by electron microscopy.

Techniques Developed for Light Microscopy Examination

With most materials, it is desirable to check polishing from time to time to see if the surface is scratch-free. Using light microscopy to check the condition of a polished surface of Pyroceram presents a problem. Not only is light reflected in a random way from those crystals on the surface but also from those below the surface and visible through the transparent, amorphous matrix. The reflections of these crystals from the surface and subsurface produce a glare that prevents detailed examination of the crystals or microstructure. Because of this normal reflected light, dark-ground illumination and reflected phase contrast are useless.

In an attempt to eliminate this troublesome glare, the samples were shadowed with chromium, but this method was time-consuming. A number of organic stains and dyes were also tried to reduce glare. Among these were Congo red, gentian violet, safranin, and Merthiolate. These stains all reduced the glare and lessened the reflections to some degree, but they each left many pools of unwanted pigment on the surface of the sample. A Sanford's marker, designed to mark laundry, was tried with success. Except when used in great excess, the marker dye left no pools of color. It could be removed by polishing the sample or by washing with alcohol, acetone, soap, and water. A blue Sanford's marker was selected for this work because the light microscope employed was corrected in the blue portion of the spectrum.

Specimen Etching

A number of etches containing hydrogen fluoride in various concentrations both with and without other acids were tried on Pyroceram. The most successful of these was composed of 5 milliliters of hydrogen fluoride, (45 percent), 5 milliliters of hydrochloric acid (concentrated), and 45 milliliters of water. This was the primary etch. To obtain greater control over etching, another etch was often used. This second etch had the same composition as the first except that methyl alcohol replaced the water. Total etching time ranged from 25 to 30 seconds. The best results were obtained by etching for 15 seconds with the first etch and then an additional 10 to 15 seconds with the second etch.

Shadowing and Replication Techniques and Processes Developed

Table I is a summary of the various replicating methods used and the results obtained. Plastic replicas of mounted Pyroceram balls were generally found to be objectionable either because the solvent for the plastic also dissolved the Lucite mount or because the plastic ripped when being removed from the sample. Faxfilm replicas, however, could be satisfactorily removed if they were flooded with methanol and then dried with a blast of cool air. This method did not work with other types of plastic replicas investigated. Preshadowed carbon or silicon monoxide replicas held so tenaciously to the surface of the sample that they had to be removed by etching. This etching not only damaged the sample, but also the replicas. The difficulty was overcome by the evaporation of a releasing agent on the sample before shadowing. Because of the time element involved in drying liquid-type releasing agents, dehydrated Victawet was selected. The Victawet was applied from a basket located directly above the sample.

Silicon monoxide replicas rather than carbon replicas were selected because they are more easily made with existing equipment and because it is easier to control the thickness of the replicas when deposited on the sample.

Because fine structure was lost in the shadows when unilateral shadowing was employed, rotary shadowing was used. Figure 2 compares the differences between a rotary shadowed sample (fig. 2(a)) and a unilaterally shadowed one (fig. 2(b)). While rotary shadowing sacrifices the sharp contrast found in unilateral shadowing, increased structural detail was obtained. In all figures the shadowing was with chromium at an angle of 30° . Silicon monoxide was the replicating agent. The entire process of shadowing and replication was carried out under vacuum conditions in the apparatus shown in figure 3. The sample was rotated at 200 rpm for each of the steps:

- (1) Victawet deposition
- (2) Shadowing
- (3) Replication

It was felt that, in view of the rather brief time that the shadowing material was brought to evaporation temperature, no slower rotational speed could be employed. Rotation during Victawet evaporation and replication tends to make these layers more uniform. After replication, the sample was removed from the vacuum chamber and immersed at an angle of approximately 30° into water at a temperature of about 100° F. The replica floated free on the surface of the water and was easy to pick up on a standard electron microscope grid.

Locating Specific Area of Specimen

There are times at which it is desirable to view a particular area or portion of the specimen. Finding a particular area when using light microscopy usually presents no problem. This is not the case in electron microscopy. In electron microscopy the replica is placed on a fine wire grid which is used to give the replica rigidity and to keep it intact when it is placed in the electron microscope. Consequently, when one attempts to find a particular area or location on the replica, the section that one may wish to see is often hidden by the wire grid.

In order to overcome this difficulty and locate a given portion of a sample for electron microscopy study, one must assume, first of all, that this area can be seen and identified using light microscopy. No special instrumentation is required in the process described here. The portion of the sample to be observed is first located under normal reflected light. The specimen is then replicated. A somewhat different replication method, however, is used than described in the previous section. Replication is made with Faxfilm shadowed with chromium, or another metal, at the desired angle. The proper thickness of silicon monoxide is then deposited in vacuum on top of the shadowed Faxfilm replica. The replica is left under vacuum until the next step of the procedure has been accomplished.

A light microscope equipped with phase contrast accessories and having a circular mechanical stage is employed. The condenser of the microscope is run as high as it will go, and a cover glass with a grid in its center is placed on the top of the condenser. An X40 phase objective is then brought with coarse adjustment into such a position as to permit focus of the grid surface. In the focusing of this grid, it may be necessary to change the elevation of the condenser slightly. One of the eyepieces of the microscope is equipped with a square-ruled graticule. Notation is then made of where one of the openings in the grid lies with respect to the lines on the square-ruled graticule. The condenser is then lowered below its optimal position.

The Faxfilm replica previously made is now taken and mounted on a microscope slide with transparent tape. Instead of facing the objective lens, the slide with the replica is inverted and made to face the condenser.

Figure 4 illustrates the relative positions of the objective, replica, grid, and condenser. The depth of focus of the X40 phase objective is sufficient to permit focusing on the replica through the supporting slide. By traversing the replica horizontally, vertically, and circularly, the proper portion of the replica can be brought to that portion of the eyepiece graticule which indicates an opening in the microscopic grid previously placed upon the cover glass. The slide is then gently

removed from the microscope, and a drop of a viscous, aqueous solution of polyvinyl alcohol is placed on the replica. The condenser is lowered to its full limit, and the objective is run up to its highest limit. The slide with the replica is then placed back into position on the microscope stage. Slowly, the condenser is brought up to the replica. When the grid on the condenser touches the layer of polyvinyl alcohol, the condenser is quickly lowered. Surface tension of the polyvinyl alcohol is sufficient to hold the grid in place while the slide is removed from the microscope. The slide is then turned so that the replica is facing up, placed in a dust-free enclosure, and left until the polyvinyl alcohol is thoroughly dry. A sharp pair of surgical scissors is used to cut excess Faxfilm from the grid.

The next step is to dissolve the Faxfilm portion of this replica. A mixture of 50 percent acetone and 50 percent ethanol (absolute) by volume is satisfactory, using a modified Jaffe technique (see appendix). When all the Faxfilm has been washed from the replica in this manner, the grid is moved to a piece of filter paper. The polyvinyl alcohol is then removed from the grid by chromatography using water as the carrier. After the replica is dry, it is suitable for examination in the electron microscope. Finding that square of the grid which contains the portion desired to be seen is a matter of the operator's choice. An example of an area in the subsurface region of Pyroceram viewed with electron and light microscopy using this method is shown in figures 5(a) and (b).

Figure 5(a) is a light micrograph of a developing fatigue crack in a Pyroceram specimen. The specimen for this micrograph was lightly etched as previously described and stained with a blue Sanford's marker. By using the method outlined in the preceding paragraphs, the area and part of the fatigue crack indicated by the arrow marked "B" in figure 5(a) are shown in figure 5(b). To yield the best contrast, the replica observed in figure 5(b) was first unilaterally shadowed and then lightly rotary shadowed.

Locating particular areas can prove to be a great asset in pinpointing initial failure in a material. The technique developed in this purpose can also be used for specimens of other materials.

SUMMARY OF RESULTS

The crystals of Pyroceram 9608, a crystallized glass ceramic, are randomly oriented and highly reflective so that standard microscopy techniques are not satisfactory for studying the material. New techniques and methods which make it possible to study the rolling-fatigue process in Pyroceram have been developed, and these are as follows:

1. A method for locating, orienting, and identifying specific areas to be viewed by the electron microscope is outlined. This method can also be used for other materials as well as Pyroceram.

2. A replication technique is described which makes use of preshadowed silicon monoxide replicas deposited after the application of a releasing agent. This procedure eliminates the difficulties encountered with plastic replicas because of their tendency to adhere to the specimen and to tear when removed.

3. A vibratory polishing technique was found to produce surfaces free of all evidences of fire-polishing, even when examined by electron microscopy.

4. A satisfactory stain (obtained from a Sanford's marker) was found that reduces the glare of reflected light when examining Pyroceram specimens with the light microscope.

Lewis Research Center

National Aeronautics and Space Administration
Cleveland, Ohio, September 2, 1961

APPENDIX - MODIFIED JAFFE TECHNIQUE

The Jaffe technique is a method for washing an unwanted plastic layer from a replica that is mounted on a grid. The grid, with the replica facing up, is placed on a copper screen that is resting in a depression of a spot plate. A proper solvent (a mixture of 50 percent acetone and 50 percent ethanol (absolute) for Faxfilm) is slowly introduced into the depression until the wire of the grid is wet. The spot plate is then covered and left alone for approximately 5 minutes. At this time the solvent is withdrawn by the use of a dropper and replaced with fresh solvent. This process of washing continues until all the unwanted plastic has been dissolved.

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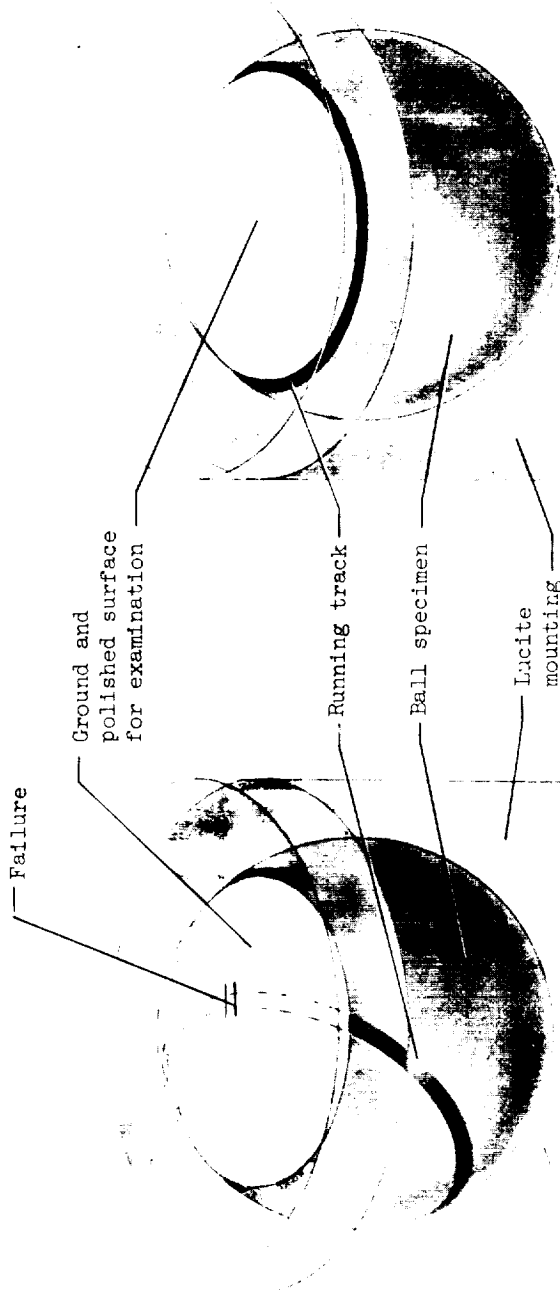
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TABLE I. - RESULTS OF REPLICATION METHODS ON PYROCERAM

Replication method	Advantages	Difficulties or disadvantages
(1) Silicon monoxide with releasing agent and pre-shadowing ^a	(a) Thickness of replica easy to control (b) Positive replica (c) Holds up well	Time-consuming
(2) Faxfilm ^a	Can be used for locating given spot on sample	(a) Demands two step process (b) Cannot be preshadowed
(3) Carbon with releasing agent and preshadowing ^a	(a) Positive replica (b) Holds up well	(a) Poor replication in poorly controlled vacuum (b) Time-consuming
(4) Silicon monoxide ^a	High resolution obtainable.	Requires "etching through" for release, which damages sample and replica
(5) Carbon ^a	High resolution	Requires "etching through" for release, which damages sample and replica
(6) Parlodion	-----	(a) Solvent attacks mount (b) Sticks too tenaciously, tends to tear
(7) Formvar	-----	(a) Solvent attacks mount (b) Sticks too tenaciously, tends to distort
(8) Polyvinyl alcohol	-----	(a) Must be removed at proper time or cannot be removed at all (b) Tends to produce excessive artifacts

^aSuitable for Pyroceram.

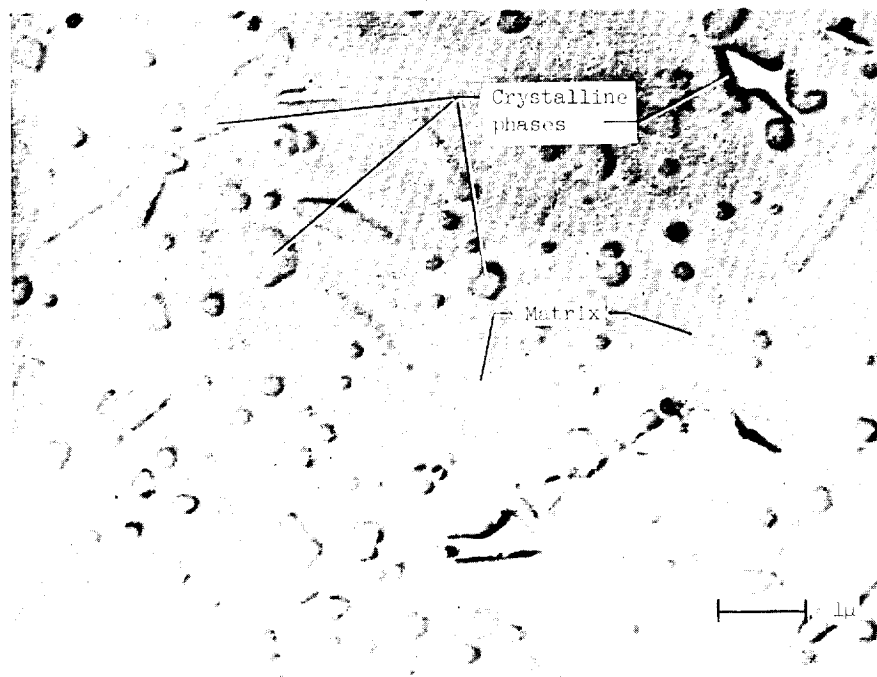


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(a) Radius to failure in track perpendicular to polishing surface.

(b) Plane of running track parallel to polishing surface.

Figure 1. - Mounting of ball specimen for examination under light and electron microscopy.



(a) Rotary shadowed.



(b) Unilateral shadowed.

Figure 2. - Electron micrographs of Pyroceram, rotary and unilateral shadowed with chromium at 30°. Sample was polished with chromium oxide on a vibrator-type laboratory polisher.

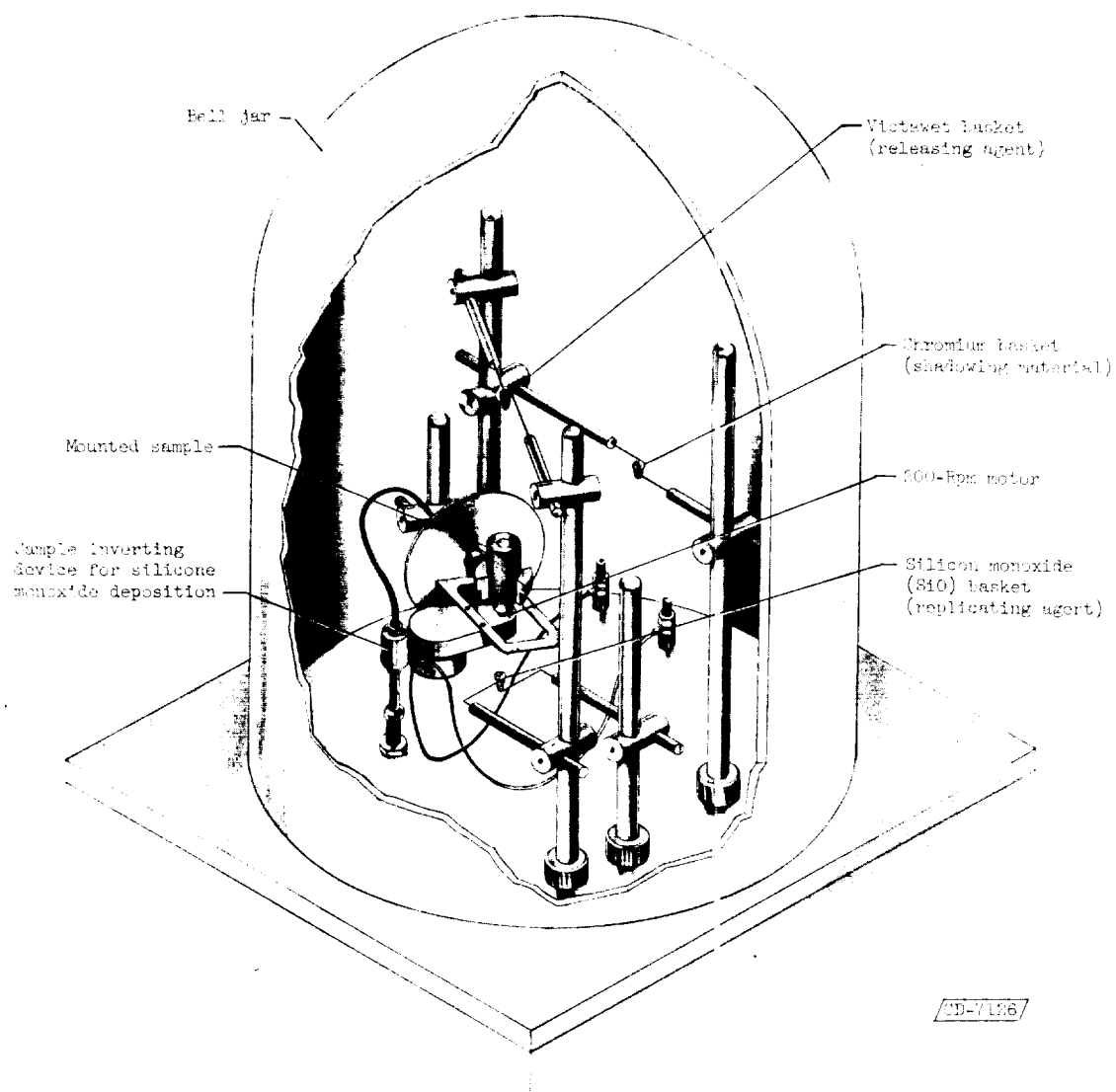


Figure 3. - Shadowing and replication apparatus. (Filament shielding has been omitted for clarity.)

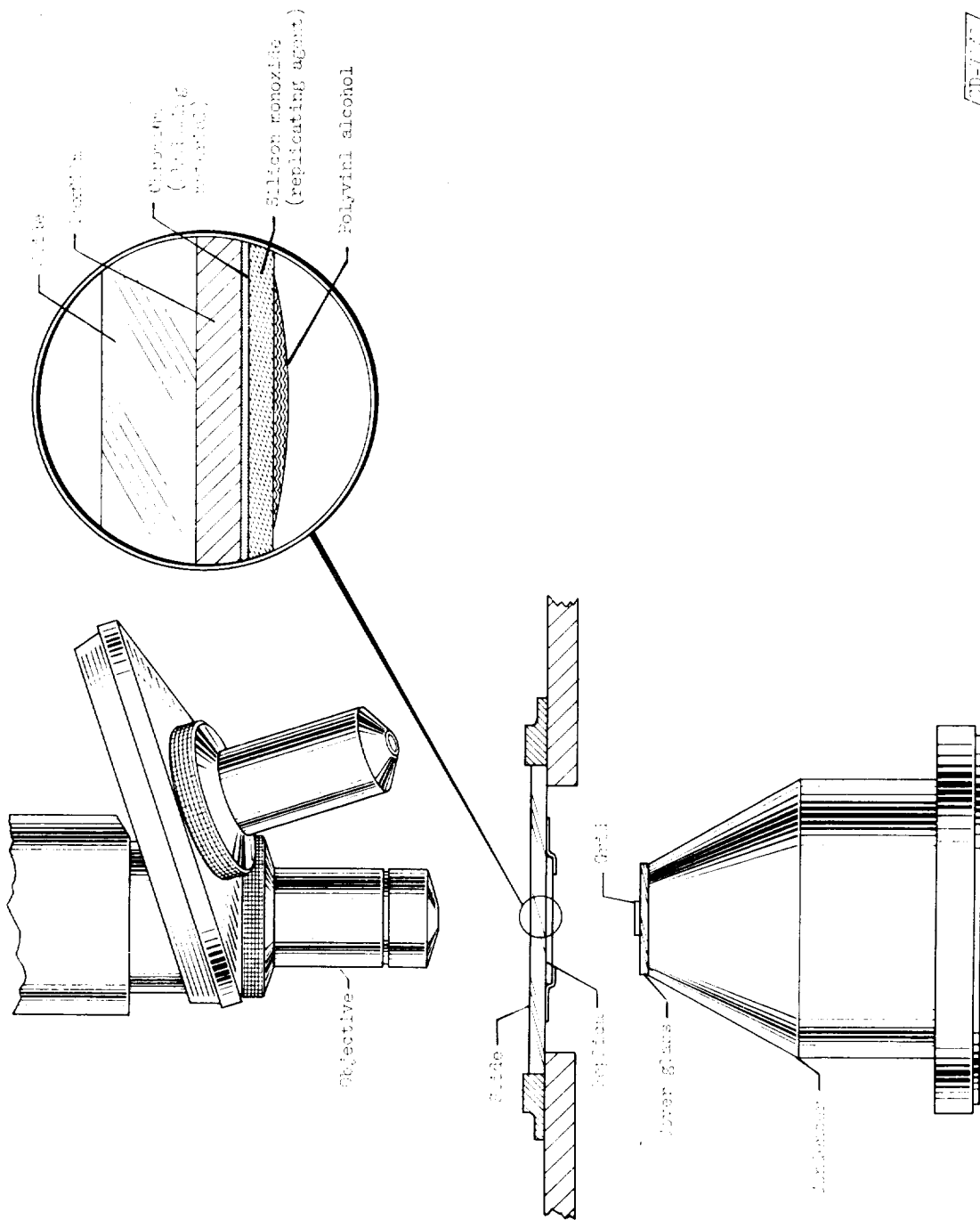
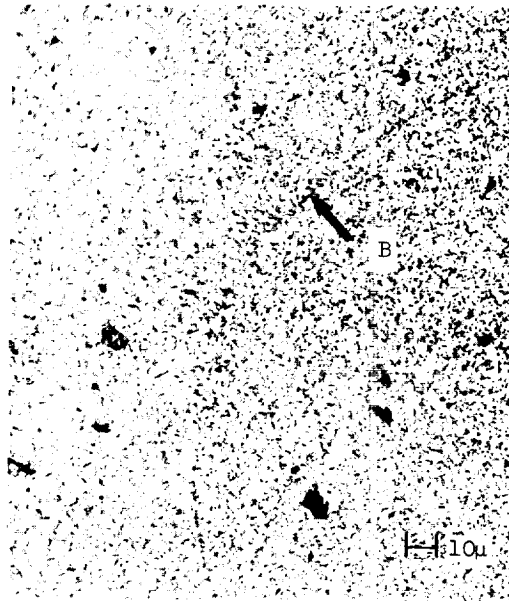
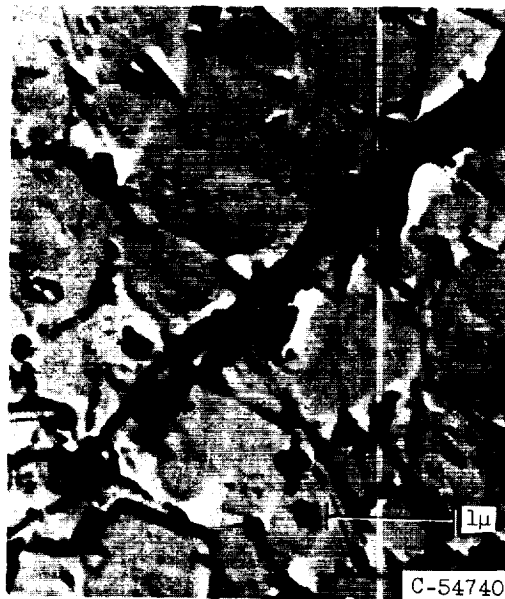


Figure 4 - Diagram for locating specific areas of specimen regions.



(a) Photomicrograph of Pyroceram lightly etched with HF + HCl. Stained with blue Sanford marker.



(b) Electron micrograph of area indicated by "B." Faxfilm-SiO replica preshadowed with chromium.

Figure 5. - Same area of Pyroceram sample as viewed by light (a) and electron (b) microscopy. "B" was located using the method outlined in the text.